

Conference Paper

Development of Magnesiant Cement Producing Technology on the Ural Region Raw Materials Basis

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Abstract

This article considers an effective way of processing natural and technogenic magnesium-containing materials, which will release magnesium oxide and magnesium sulphate for the production of magnesiant cement. Using this method, pure magnesium oxide, magnesium sulphate and magnesium sulfate have been obtained, the study considers the properties of magnesiant cement with differeng magnesium oxide production conditions.

Keywords: non-conventional magnesium containing raw materials, technogenic materials, magnesiant cement, hydrochemical processing, ammonium hydrosulfate.

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At present, the main type of binder for fire-resistant building materials is calcium cement - portland, alumina, high alumina. This is due to both technological and economic reasons, the most important of which are setting times and high strength, as well as availability and relatively low cost. Alternative binders are phosphate, silicate, magnesia and organic binders. Each of these binders has its own disadvantages, which reduce their popularity. For phosphate binders, the main disadvantage is the need for heat treatment to achieve initial mechanical strength and water resistance; for silicate binders, the presence of a significant number of alkalis and, consequently, low fire properties of materials; For magnesiant (sulphate - chloride) binders it is a limited availability of magnesiant cement, relatively low water resistance when using low-quality binders and temperature range of dishardening 450 - 900 °C, associated with the decomposition of hydrate compounds.

Meanwhile, the systematic increase in the cost of cements, both domestic and imported, prompts to look for alternative binders with a similar set of properties. One of the ways to solve this problem can be a complex magnesia-phosphate binders. Magnesiant cement (magnesium oxide + chloride / magnesium sulfate) hardens well under normal conditions with the formation of a strong cement stone, and phosphates

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show high strength properties, including the lack of dishardening, when heated above 350 °C, while ensuring water resistance of the system.

The low availability of active magnesium oxide prevents the wide spread of magnesia binder. There are several producers of magnesium oxide in Russia: OJSC "Magnesite Plant", which gradually reduces the volume of caustic magnesite supplied due to changes in the technology of production of sintered powders; LLC "Vyazma-Brusit" processing crystalline brusite ($Mg(OH)_2$) of Kuldura deposit, requiring additional heat treatment and OJSC "Kaustik", Volgograd, producing small amounts of magnesium oxide from natural bishofit. Import of dispersed magnesium oxide in the form of burnt magnesium is carried out from Mexico, Israel, China and other countries, and is up to 60% of the market.

One of the ways to solve the problem of the lack of active magnesium oxide in the domestic market can be the development of cost-effective technology for obtaining magnesium products (hydrocarbonate, magnesium oxide and magnesium sulphate) from natural and/or man-made magnesium-containing materials by hydrochemical enrichment [1, 2].

The authors propose a technology of complex processing of industrial and/or natural magnetic materials production wastes with the use of regenerated leaching sulfuric acid solution - ammonium hydrosulfate solution. The main mass of technogenic magnetic-containing waste in Russia today is represented by asbestos and chromite ore production wastes - serpentinite, dunite and products of their regeneration. Typical chemical and phase composition of such products is presented in Tables 1 and 2, respectively.

TABLE 1: Chemical composition of serpentinite, wt. %

MgO	SiO ₂	Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃	FeO	CaO	NiO	MnO	Na ₂ O	K ₂ O	CO ₂
41,1	41,3	0,67	0,49	11,1	2,22	0,43	0,29	0,27	0,01	0,04	0,77

TABLE 2: Mineralogical composition of serpentinite, wt. %

Antigorite	Lizardite	Magnetite	Bastite
50-85	до 25	1-5	до 10

The proposed technology includes

1) Sulphuric acid leaching of raw materials with ammonium hydrosulphate solution and extraction of magnesium and iron oxide into the solution by the following reactions:

For magnesium silicates:



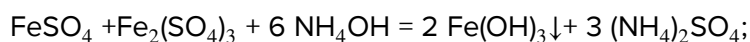
For magnetite:



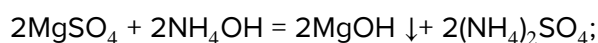
In addition to the basic minerals, there are impurities in the pulp: Al, Zn, Mn, Ni, Co, Pb, Na, K, and others which, as a result of reaction, pass to sulphates of corresponding metals and are in the soluble form.

2) Filtration of acid-resistant residue containing RO_2 , R_2O_5 oxides for subsequent use as a raw material for the production of building materials, refractories, ceramics, abrasives, etc;

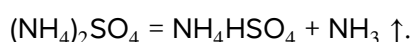
3) Iron deposition from ammonia solution and separation of iron hydroxide III for further use in the production of pigments;



4) Magnesium precipitation from ammonia solution and separation of magnesium hydroxide for further use as a raw material;



5) obtaining a pure solution of ammonium sulfate from which crystallites' ammonium sulfate is extracted; which is thermally decomposed into ammonium hydrosulfate and ammonia by reaction according to the technology developed and tested on a pilot industrial installation:



6) return of the obtained ammonium sulfate and ammonia into production.

Part of the purified magnesium sulphate solution was dried at a temperature of 110 °C to full crystallization to obtain crystalline hydrates $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$. The product obtained after drying contains, wt. %: MgO - 17,1; SO_3 - 35,1; CaO - 0,01; Fe_2O_3 - 0,0002; SiO_2 - 0,0005; content of insoluble substances in water - 0,08. After sedimentation of purified magnesium hydroxide, the sludge is sedimented, decanted and washed. Drying and thermal treatment of hydroxide was carried out in laboratory furnaces at the temperature of 450 - 800 °C until the mass loss was stopped. The product obtained after calcination co-presents, wt. %: MgO - 99,6; R_2O - 0,11; CaO - 0,12; Fe_2O_3 - 0,04; SiO_2 - 0,09. Specific surface of the material was 4750 m^2/g , average particle size - 3.5 μm .

To obtain the magnesia binder, the magnesium hydroxide was thermally treated at temperatures of 480 and 760 °C until the mass loss was completely stopped. Magnesian binder was obtained from magnesium oxide glued with magnesium sulphate and sodium tripolyphosphate solution in ratio 10 / 1 with density of 1, 2 g/cm^3 up to humidity of 70-75 %.

Tests to study the setting time of the magnesia binder were carried out on a cement test. The setting time, apparent density and compressive strength of the obtained samples were determined according to GOST 30744-2001. "Cements Methods of testing

with using polyfraction standard sand". Setting times determination results for magnesia cement paste are presented in Table 3.

TABLE 3: Setting times for the magnesia binder

Setting times	From oxide, heat-treated at, °C	
	480	760
Initial set, min	6	11
Final set, min	17	27

The apparent density of samples from magnesia cement was, g/cm³: 1.75-1.80 for the test obtained from oxide fired at 480 °C and 1.95-2.0 for the test obtained from oxide fired at 760 °C.

Oxide (not less than 95 wt. % MgO) and sulfate (not less than 98 wt. % MgSO₄·6H₂O) of magnesium obtained by this method allow to obtain magnesia binder with daily strength of 5 – 7 MPa, 28 daily strength - up to 20 MPa (Figure 1). Introduction of phosphate salts allows, on the one hand, to provide water resistance of the magnesia binder, on the other hand, to eliminate the dishardening of the complex binder when heating above 450 °C.

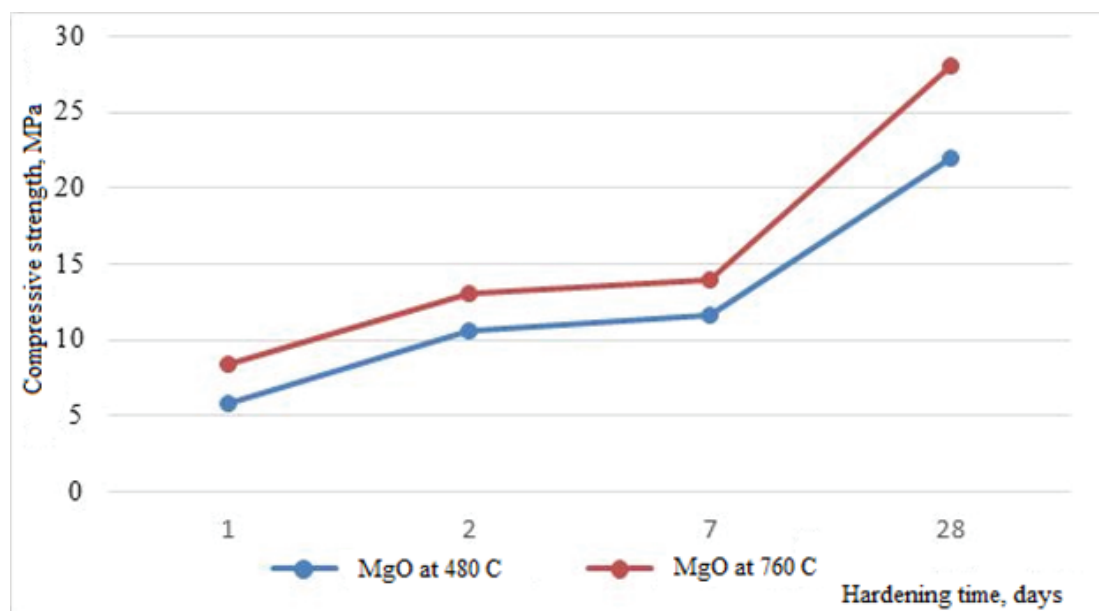


Figure 1: Hardening time influence on compressive strength

When mixing magnesian binder with magnesium sulfate solutions - MgSO₄, complex compounds - magnesium hydroxysulphates are formed at the first stage of hardening of magnesian binder: magnesium pentahydroxysulphate - 5Mg(OH)₂MgSO₄·3H₂O and further at the second stage trihydroxysulphate magnesium - 3Mg(OH)₂MgSO₄·8H₂O is formed.

1. Conclusions

Test results show that lower temperature burned magnesium oxide paste has shorter initial time, which indicates a higher activity of the "low-burned" powder.

Developing a pure magnesium oxide and other products from magnesium sulfate producing technology based on the Ural region raw materials including serpentinite, dunite was shown to be possible, an energy- and resource-efficient technology will allow to produce high-purity powder MgO and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, and obtain a magnesian binder with a high level of physical and mechanical properties.

References

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